Enclosure 1b. Category 1 Application form – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in English on the website
https://www.vscentrum.be/en/access-and-infrastructure/project-access-tier1

Title of the application:

Ab initio molecular dynamics study on the role of water in the reaction mechanism during methanol conversion in H-SAPO-34

Name and first name of the applicant:

Bailleul Simon

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

Ir. / PhD Fellow

e-mail address:

Simon.Bailleul@UGent.be

Total computing time that is needed, in node days:

4880

Total disk storage that is applied for (in GiB):

656 GiB scratch space – ~1 TB long-term storage (provided by UGent)

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

Due to the growing relevance of renewable resources, interest in the methanol-to-olefin (MTO) process has grown since it is one of the most prominent technologies to bypass crude oil in light olefin, i.e. ethylene and propylene, production. For this process, the chabazite structured catalyst H-SAPO-34 is of particular interest because of its high selectivity towards light olefins. [1] In view of the development of conversion processes using biomass feedstock, the methanol feed may contain a significant amount of water. Therefore, it is relevant to analyze the influence of water on the methanol conversion over H-SAPO-34 as there are experimental indication that water alters product selectivity and enhances catalyst lifetime. [2] Furthermore, the adsorption behavior of water and methanol in H-SAPO-34 has already been investigated with molecular dynamics simulations, showing a pronounced influence on the framework flexibility and proton mobility. [3] What is still missing, is insight in the effect of water on the individual reaction steps in the proposed MTO mechanisms, namely the side chain and paring mechanism depicted in **Figure 1a**. Indeed, water may act as assisting or spectator molecule during elementary reaction steps. Gaining detailed knowledge on this matter will help in the optimization of the MTO process for biomass based feedstock. Therefore, this study will focus on unraveling the influence of the presence of water on the methanol reactivity at a molecular level. To this end, molecular dynamics simulations at realistic process conditions (623 K and 1 atm) will be conducted.

During this project, the effect of water will be taken into account by comparing dynamic simulations at low (1 water guest molecule) and high (9 water guest molecules) water content, as represented in **Figure 1b**. First, the stability and the water interaction of 8 different intermediates in the MTO mechanisms, depicted in **Figure 1a**, will be analyzed using molecular dynamics (MD) simulations. Once these systems have equilibrated for 50 ps, metadynamics (MTD) simulations will be performed to unravel the transition paths between the different intermediates. Via these MTD simulations, the free energy surface (FES) of the MTO reactions is reconstructed and kinetic and thermodynamic data can be derived from the FES. Finally, to validate the reliability of the results obtained via the MTD simulations, a detailed committor analysis will be performed by generating hundreds of MD paths from the obtained FES.

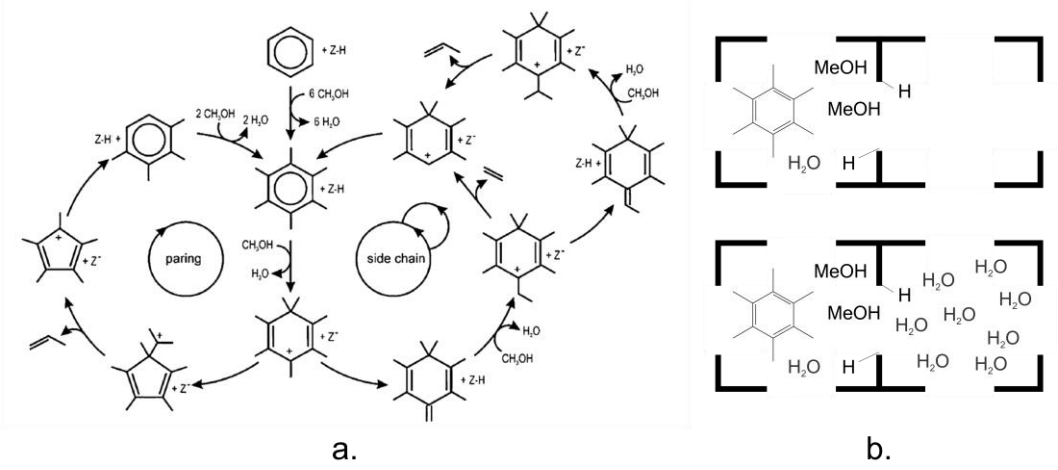

Figure 1. Schematic representation of the reaction mechanisms proposed for the MTO process (a) and the low and high water content simulations used to analyze the effect of water (b). Taken from ref [4].

[1] J. Q. Chen, A. Bozzano, B. Glover, T. Fuglerud, and S. Kvisle, "Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process," *Catal. Today*, vol. 106, no. 1–4, pp. 103–107, Oct. 2005.

[2] A. J. Marchi and G. F. Froment, "Catalytic conversion of methanol to light alkenes on SAPO molecular sieves," *Appl. Catal.*, vol. 71, no. 1, pp. 139–152, Apr. 1991.

[3] K. De Wispelaere, B. Ensing, A. Ghysels, E. J. Meijer, and V. Van Speybroeck, "Complex Reaction Environments and Competing Reaction Mechanisms in Zeolite Catalysis: Insights from Advanced Molecular Dynamics," *Chem. – Eur. J.*, vol. 21, no. 26, pp. 9385–9396, Jun. 2015.

[4] D. Lesthaeghe, A. Horré, M. Waroquier, G. B. Marin, and V. Van Speybroeck, "Theoretical Insights on Methylbenzene Side-Chain Growth in ZSM-5 Zeolites for Methanol-to-Olefin Conversion," *Chem. – Eur. J.*, vol. 15, no. 41, pp. 10803–10808, 2009.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 12 of this application form.

No abstract of this work may be published on the website (see item 12)

Recently, the methanol-to-olefin (MTO) process received a growing interest as one of the most prominent technologies to bypass crude oil in the production of light olefins. H-SAPO-34 is an important industrial catalyst for this process due to its high selectivity to light olefins. Nowadays, reaction mechanisms based on hydrocarbon pool (HP) species, which co-catalyze the reactions, have been generally accepted. The question how water, a byproduct of methanol synthesis and the MTO process itself, influences the methanol conversion reactions over H-SAPO-34 however remains up to date unanswered. In this project, this issue will be addressed at a molecular level using advanced dynamic techniques. The gained knowledge will help to determine the optimal methanol-water ratio in the feed and in the further optimization of the MTO process.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 3 “EasyChair proposals submission procedure”).

European Research Council under the European Union’s Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

5. Name and email address of the promoter(s) of the research project:

Prof. dr. ir. Veronique Van Speybroeck (Veronique.VanSpeybroeck@UGent.be)

6. Persons mandated by the Applicant to compute on the Tier-1 within the framework of the present project: Please provide for every person:
   - name and first name
   - institution
   - research group / department
   - title / position
   - experience of using HPC resources in the past (Tier-0/Tier-1/Tier-2 infrastructure in Belgium and abroad)

Ir. Simon Bailleul
Ghent University, Center for Molecular Modeling
ERC PhD fellow
4 months of experience with TIER1 at Ghent University
1 ½ year of experience with TIER2 at Ghent University

Ir. Pieter Cnudde
Ghent University, Center for Molecular Modeling
PhD fellow
1 year of experience with TIER1 at Ghent University
2 ½ year of experience with TIER2 at Ghent University

Dr. ir. Jeroen Van der Mynsbrugge
Ghent University, Center for Molecular Modeling
BOF Post-doc
2 years of experience with TIER1 at Ghent University
6 ½ year of experience with TIER2 at Ghent University

Prof. dr. ir. Veronique Van Speybroeck
Ghent University, Center for Molecular Modeling
Full Professor
2 years of experience with TIER1 at Ghent University
6 ½ year of experience with TIER2 at Ghent University

7. Explain why this project needs to run on a Tier-1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

The application of advanced molecular dynamics simulation methods to unravel reaction mechanisms and kinetics of catalytic reactions is a flourishing research field. The Center for Molecular Modeling was among the first research groups which succeeded in applying metadynamics (MTD) to elucidate the kinetics of zeolite-catalyzed reactions (Moors, S. L. C. et al. ACS Catal. 2013, 3, 2556; Van der Mynsbrugge, J. et al. ChemCatChem 2014, 6, 1906; De Wispelaere, K. et al. Chem. Eur. J. 2015, 21, 9385). To maintain its prominent position in this highly competitive field by making high-impact contributions, access to the highly efficient TIER1 infrastructure, with its fast nodes and inter-nodal communications, is indispensable.

To perform all simulations proposed in this study, a computing time of over 4000 node days will be needed to obtain accurate statistical averages from the molecular dynamics simulations and converged free energy surfaces from the MTD simulations. To complete this project in an acceptable timeframe, multi-node jobs are required, which makes the ability to run a large amount of jobs simultaneously on the TIER1 infrastructure essential for the speedup of this research.

8. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed.
   Indicate for each typical computing task the required resources:

   - wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
   - memory (maximum 64 GiB/node)
   - number of nodes
   - number of CPU cores
   - disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier-2 DATA/HOME partitions and the Tier-1 SCRATCH partition
   - number of tasks, and an indication of how many such tasks would be submitted concurrently.

   This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of

actual calculations on Tier-1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.

(max. 1 A4 Arial 12).

During this study, three types of ab initio molecular dynamics (AIMD) simulations will be performed using the CP2K software package on systems consisting of approximately 200 atoms. The computational requirements for this study have been carefully considered based on test simulations on the systems under study performed on the TIER2 (delcatty cluster) and TIER1 infrastructure at Ghent University.

Calculation flow:

1. **Molecular dynamics (MD)** simulations in the NPT ensemble at 623 K and 1 atm for 50 ps are performed to evaluate the stability and interaction with water of 8 intermediates of the side chain and paring mechanism. Sufficiently long simulations are required to obtain an equilibrated system and accurate statistical averages. MD simulations of similar systems on TIER1 have shown that 5 ps simulations require approximately 3 node days. Therefore, it is expected that each of these simulations will require about **35 node days** (multi-node jobs on 2 nodes), taking into account the equilibration before the 50 ps production run. Since each intermediate needs to be evaluated at both low and high water content to assess the effect of water, **16 MD jobs** will be performed.
2. To analyze the transition between intermediates, **metadynamics (MTD)** simulations in the NVT ensemble at 623 K will be performed. For this type of simulations convergence is typically attained in 100 – 200 ps, depending on the height of the free energy barrier of the reaction and the number of collective variables. Similarly as for the MD simulations, a simulation of 5 ps can be performed in approximately 3 node days, so each simulation is expected to take up to **120 node days** (multi-node jobs on 2 nodes). Since each intermediate serves as a reactant state for an elementary reaction in the reaction mechanism, this amounts again to a total number of **16 MTD jobs**.
3. A **committor analysis (CA)** will be performed to assess the quality of the results obtained from the MTD simulations, by generating hundreds of AIMD paths starting from the trajectory of **each of the 16 MTD runs**. Based on test simulations performed on TIER2

(delcatty cluster), the time to generate 1 path is estimated to be about **18 node hours** for systems with unit cells as large as H-ZSM-5 (another archetypal MTO catalyst). To obtain sufficient sampling for statistical relevant results, it is estimated that at least **200 paths** will have to be generated for each of the MTD runs.

Table 1 summarizes the estimated node and core days required for each simulation type:

Table 1. Estimated core and node days required for the project.

Job type	# of simulations	Node days per simulation	Total node days	Total core days
MD	16	35	560	8960
MTD	16	120	1920	30720
CA	16	200 x 0.75	2400	38400
			4880	78080

Table 2 summarizes the requirements for scratch space and long-term storage for each simulation type. Because of the long simulation times, a complete MD or MTD trajectory cannot be obtained within the wall time limit of 72 hours, but requires several restarts. As a result, the scratch volume per MD of MTD simulation is relatively low.

Table 2. Estimated scratch space and long-term storage requirements for the project.

Job type	Scratch [GB/run]	Long-term storage [GB/run]	Total scratch [GB]	Total long-term storage [GB]
MD	0.5	7.5	16 x 0.5 = 8	16 x 7.5 = 120
MTD	0.5	15	16 x 0.5 = 8	16 x 20 = 240
CA	0.2	0.2	16 x 200 x 0.2 = 640	16 x 200 x 0.2 = 640
			656	1000

9. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

   - a reference to the software's web page
   - the software license system (open source, GPL, etc.)

- if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier-1 by the Applicant (+ add a copy of the signed license)
- if need be, which license server will be used (name + IP address)
- whether the software is already available on the Tier-1 (see https://www.vscentrum.be/cluster-doc/software/tier1-muk) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier-2 installation)

The CP2K software package (http://www.cp2k.org/) will be used to perform the molecular dynamics simulations. This package is freely available under the GPL license and the required version (CP2K/20130228-ictce-4.1.13) is already available on TIER1.

Provide the results of scaling tests that were conducted with this software, preferably on Tier-1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.
Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

A scaling test for the CP2K software package on TIER1 has been conducted using one of the systems which will be studied, namely hexamethylbenzene, 2 methanol molecules and 9 water molecules adsorbed in H-SAPO-34 at 623 K and 1 atm. Short NPT runs (100 steps) have been performed on 16, 32, 64 and 128 cores on the TIER1 cluster for which the results are summarized in **Table 3**. Furthermore **Figure 2** shows the speedup normalized to the 16 core simulation for these simulations. This graph indicates that the use of more than 2 nodes does not efficiently speed up the simulation.

Table 3. Summary of the scaling test of the CP2K software package on TIER1 using hexamethylbenzene, 2 methanol molecules and 9 water molecules adsorbed in H-SAPO-34 at 623 K and 1 atm as a model system.

# nodes	# cores	Absolute timing (s)	Speedup	# cores x timing
1	16	3066.8	1.0000	49068.4672
2	32	1652.6	1.8558	52882.2432
4	64	1033.5	2.9675	66141.696
8	128	771.1	3.9769	98706.9824

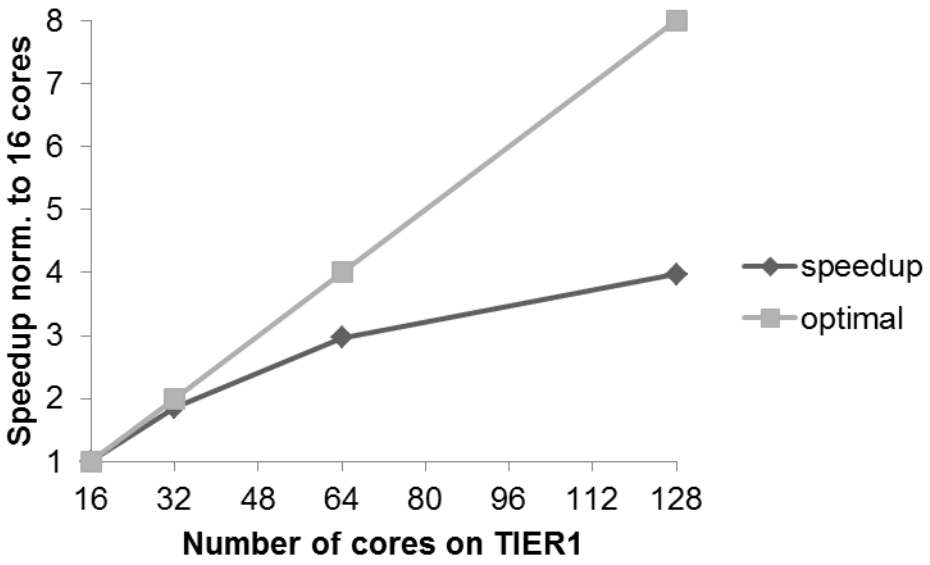

Figure 2. Speedup normalized to 16 cores for an NPT MD simulation of hexamethylbenzene, methanol and water in H-SAPO-34 at 623K and 1 atm with CP2K on TIER1 with 1-8 nodes.

10. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts, …)?

We estimate the proposed simulations can be completed over a time period of approximately **6 months**, preferably **starting in March 2016**. Similar usage on a monthly basis is expected.

This estimated timeframe takes into account the actual runtime of the simulations, as well as intermediate data analysis tasks and frequent job restarts.

11. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier-1 system, as well as other Tier-1 and Tier-0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier-1 or on other Tier-1 or Tier-0 supercomputers. DOI links are sufficient.

List of granted research projects of the Flemisch TIER1 system:

- Molecular dynamics study of pentene in H-ZSM-5: towards a better estimate of adsorption enthalpies (J. Van der Mynsbrugge – 1824 node days – 07/03/2014 – 06/07/2014)
- Dynamical kinetic study of zeolite catalyzed reactions (K. De Wispelaere, 4371 node days, 07/07/2014 – 31/12/2014)

- Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations (J. Van der Mynsbrugge, 4864 node days, 01/01/2015 – 30/06/2015)
- Characterizing adsorption properties of C_4 – C_6 alkenes on H-ZSM-5 using molecular dynamics simulations (P. Cnudde, 4260 node days, 13/07/2015 – 31/12/2015)
- Dynamical first principle benchmark studies on alkene methylation in H-ZSM-5 (K. De Wispelaere, 1400 node days, 01/12/2015 – 30/06/2016)

List of scientific output within the framework of granted computing time:

- Suppression of Aromatic Cycle in Methanol-to-Olefins Reaction over ZSM-5 by post-synthetic modification using Calcium, I. Prokopyeva, S. Bailleul, A. Pustovarenko, J. Ruiz-Martínez, K. De Wispelaere, J. Hajek, B.M. Weckhuysen, K. Houben, M. Baldus, V. Van Speybroeck, F. Kapteijn, J. Gascon, ACS Catalysis, Submitted 2016
- Towards molecular control of elementary reactions in zeolite catalysis by advanced molecular simulations mimicking operating conditions, K. De Wispelaere, S. Bailleul, V. Van Speybroeck, Catalysis Science & Technology, Submitted 2015
- Insight in the effect of water on the methanol-to-olefins conversion in H-SAPO-34 from molecular simulations and in-situ micro-spectroscopy, K. De Wispelaere, C.S. Wondergem, B. Ensing, K. Hemelsoet, E.J. Meijer, B.M. Weckhuysen, V. Van Speybroeck, J. Ruiz-Martinez, ACS Catalysis, Submitted, 2015
- http://dx.doi.org/10.1002/chem.201500473
- http://dx.doi.org/10.1016/j.jcat.2015.01.013
- http://dx.doi.org/10.1002/cctc.201402146
- http://dx.doi.org/10.1021/cs400706e
- http://dx.doi.org/10.1039/c4mh00127c
- http://dx.doi.org/10.1039/C3CP54132K

12. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the FWO / Flemish Supercomputer Center.

Yes

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
Associatie KU Leuven: hpcinfo@kuleuven.be
Associatie Universiteit Gent: hpc@ugent.be
Associatie Universiteit Hogescholen Antwerpen: hpc@uantwerpen.be
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For the other institutions: caroline.volckaert@FWO.be